Release of Mercury Vapor from Coal Combustion Ash

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INTRODUCTION

The goal of the research described in this manuscript was to determine and quantitate mercury vapor release to the environment from various coal combustion by-products. Research has been done on enhancing the removal of mercury from flue gas, which often leaves the removed mercury in the coal combustion by-products (CCBs). Little research has been done, however, on determining the fate of mercury in CCBs, especially vapor transport. Some researchers have predicted a high potential for significant offgassing of mercury from CCBs. Prior research done at the University of North Dakota Energy & Environmental Research Center (EERC) on thermal desorption of mercury from CCBs has indicated, however, that there may not be a significant tendency for mercury to offgas from dry disposed CCBs. This work done at temperatures from ambient to 600°C indicated little tendency for mercury offgassing at temperatures below about 250°C.

Six CCBs were chosen for use in this research. The samples were those submitted by members of our Coal Ash Resources Research Consortium (CARRC, °®±² ±«² ½ ¼½®) members. The ash used consisted of two Powder River Basin subbituminous ashes, two eastern bituminous ashes, and two South African ashes. The ash identities and mercury contents are summarized in Table 1.

Table 1. Ash Description with Total Mercury Content

Ash Sample	Coal/Ash Description	Total Mercury Content, µg/g
99-188	PRB subbituminous fly ash + FGD material	0.112
99-189	PRB subbituminous + petroleum coke fly ash	0.736
99-692	Eastern bituminous fly ash	0.140
99-693	Eastern bituminous fly ash	0.268
99-722	South African fly ash	0.638
99-724	South African fly ash	0.555

One criteria for CCB selection was the need for a relatively high mercury content. It was decided that a mercury content and CCB total mass that would allow for the accurate determination of 1% of the total mercury in the vapor phase was a good starting point. Many of the ash samples in our ash inventory have extremely low mercury concentrations. The ash samples used in these experiments had some of the highest mercury concentrations of all of the ashes in our CARRC inventory.

EXPERIMENTAL

Tall, wide-mouth 250-mL bottles with bonded Teflon™ liner caps were used for the mercury offgassing experiments. The caps had two holes drilled in them for inlet air and for outlet air containing any mercury from CCBs in the bottles. A 100-g aliquot of each sample was placed and compacted into the container shown in Figure 1. Two sets of samples were set up to compare and contrast the release of mercury at ambient and near-ambient temperatures. A gas stream of breathing quality air was introduced at the top of the container through a gas inlet in the cap. This caused the container to become slightly pressurized and forced air through the ash at the bottom. The air passed through the ash and was vented to a trap to collect any mercury released. The outlet of the container was a glass tube in the center of the sample that terminated several millimeters from the bottom of the container. Glass wool and a 0.45-μm Teflon™ filter prevented ash from escaping with the air. Any mercury released from the ash was trapped on the gold-coated quartz analytical trap shown in Figure 1. The second gold-coated quartz guard trap was present to prevent any mercury in the surroundings from entering the system. Inlet mercury traps were positioned on each container to clean the inlet gas of mercury prior to introduction to the sample.

The tubes containing the gold-coated quartz traps were blanked by thermal desorption at approximately 550°C before accumulation of mercury from the samples began. Argon was passed through the ambient temperature samples for 2 days. The analytical traps were then thermally desorbed by heating the tube to 550°C. Atomic fluorescence was used to detect any initial mercury release. Data collection was done both on the atomic fluorescence detector and simultaneously through a Hewlett Packard 3393A integrator for a more permanent record. The effluent mercury from the atomic fluorescence detector was then collected in an impinger containing 20 mL of a 4% permanganate in 10% sulfuric acid solution. This was done in case a large mass of mercury too great for the atomic fluorescence detector would be emitted. After collection of mercury, 10% hydroxyl amine sulfate solution was added to decompose any remaining potassium permanganate. This additional precaution was found to be unnecessary but was continued as a precaution throughout the entire experiment. This initial 2-day experiment was done to determine what equilibration time might be sufficient for mercury offgas determinations over longer time periods. With no readable signal, it was decided to try 90-day equilibration periods for the duration of the experiment.

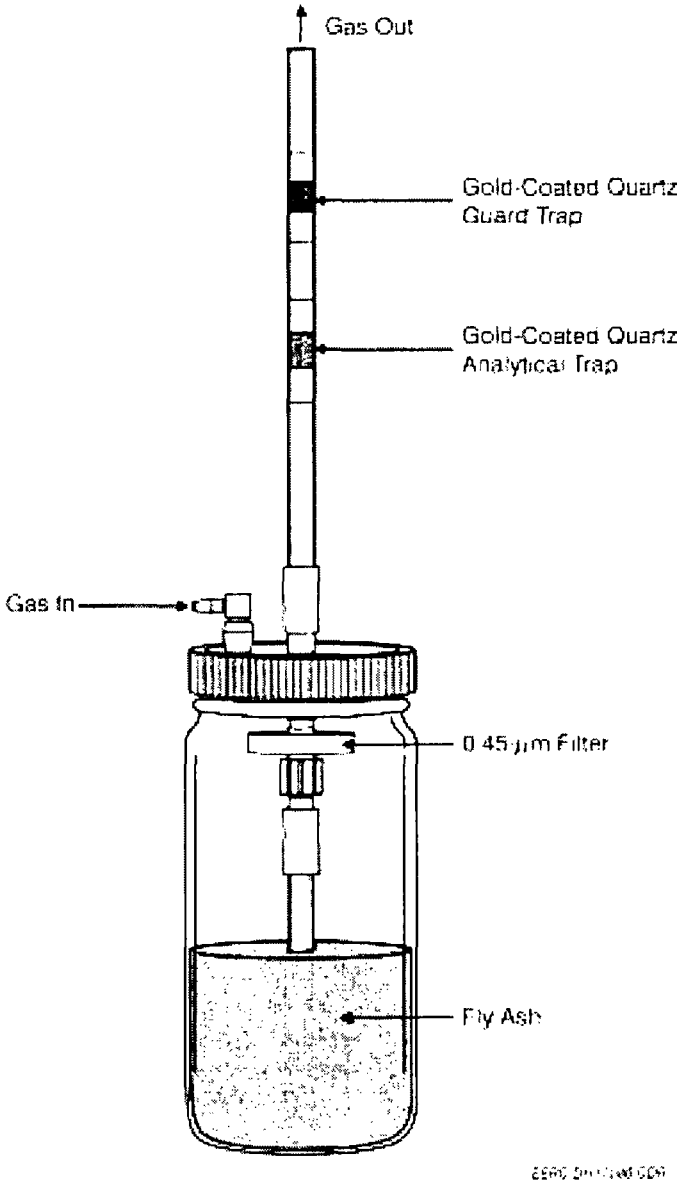

Figure 1. Apparatus used for mercury offgassing experiments.

Breathing quality air was used for the duration of the experiment. A flow rate of 1 mL/min was the target gas flow; however, 1 to 4 mL per minute was actually achieved.

The near-ambient samples were set up by placing containers in a 37°C heated sand bath. This sample set and the ambient sample set shared the same gas stream from a common gas manifold.

RESULTS AND DISCUSSION

The initial, 2-day thermal desorption of the ambient sample set yielded a very small peak for only Sample 99-188. All samples indicated that some mercury was released after 90 days. The chromatographs indicated low picogram levels of mercury. The results of all of the testing periods are shown in Tables 2 and 3. The value for N 99-188 is an estimate; the signal was over the atomic fluorescence instrument range and has not been confirmed.

The impingers were not analyzed for mercury because of the very low emission rates indicated by the atomic fluorescence determination

Table 2. Ambient Temperature Results in Picograms of Mercury per Gram of Ash

Sample	2 days	90 days	55 days	26 days	90 days	Total – 263 days
A 99-188	0.059	1.439	0.142	0.011	4.245	5.896
A 99-198	<0.001	0.489	0.133	<0.001	4.501	5.123
A 99-692	<0.001	0.953	<0.001	<0.001	3.167	4.120
A 99-693	<0.001	0.648	<0.001	<0.001	4.980	5.628
A 99-722	<0.001	1.619	0.033	<0.001	6.878	8.530
A 99-724	<0.001	0.240	0.007	<0.001	6.071	6.318

Table 3. Near Ambient Temperature Results in Picograms of Mercury per Gram of Ash

Sample	90 days	10 days	26 days	90 days	Total – 216 days
N 99-188	26.369*	0.840	<0.001	3.542	30.751
N 99-189	0.024	<0.001	<0.001	9.307	9.331
N 99-692	0.142	<0.001	<0.001	11.191	11.333
N 99-693	0.855	<0.001	<0.001	3.448	4.303
N 99-722	0.003	<0.001	<0.001	5.636	5.639
N 99-723	2.059	<0.001	<0.001	5.852	7.911

* Over instrument range.

CONCLUSIONS

No pattern was evident to link the total amount of mercury determined through bulk analysis to the release of mercury vapor. This is evident because Sample 99-188 had the lowest total mercury content but released the highest amount of mercury vapor over the course of the experiment. Experiments are continuing to determine long-term release of mercury from CCBs to confirm the results of this experiment. It is thought that the higher values of emitted mercury for the last equilibration period were due to

saturation of the inlet mercury trap with accumulation of a large blank from the gas stream. The experiments are being repeated to confirm or refute this hypothesis.

The average release of mercury from the ambient temperature samples was 5.936 pg/g or 0.023 pg/g/day. The average release of mercury from the near ambient samples was 7.703 pg/g or 0.036 pg/g/day. These values include the higher concentrations seen during the last 90-day period. The near ambient average does not include the value for N 99-188 because the value is suspect and has not been confirmed. The release of 0.023 pg Hg/g CCB/day and 0.036 pg Hg/g CCB/day in the ambient and near ambient temperature samples respectively would equate to 1.810^{-8} lb Hg/ton CCB/yr and 2.610^{-8} lb Hg/ton CCB/yr respectively. An overall average from both sets of experiments is 2.210^{-8} lb Hg/ton CCB/yr, a very small mass of mercury. To put this into context, if one were to apply this figure to a coal-fired power plant with an annual production of 200,000 tons of ash per year, there would be a potential maximum release of 0.0044 pounds of mercury per year. This is equivalent to 2.00 grams of mercury.

Will the mercury removed from the flue gas really be removed from the environment or will it be released later as mercury vapor? Currently, all studies indicate that a minute amount of mercury vapor is released into the environment from the disposal of CCBs. As the control of mercury air emissions from coal-fired power plants improves and more mercury is contained in the CCBs, this question will need to be reevaluated.

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